Abstract

The study of adsorption of n-alkanes in zeolite pores represents both a fundamental problem in molecular thermodynamics and also a problem with substantial industrial importance. Until mid 19th century, adsorption was mainly used for purification processes such as removal of H_2S and mercaptans from natural gas and organic matter from water. However, with the emergence of molecular sieves, especially zeolites, adsorption processes have become an attractive alternative to distillation in large scale separation of mixtures that have low relative volatility into streams each enriched in one of the components. The pore diameters of molecular sieves are of the order of molecular diameters and hence selective adsorption can be achieved by both a difference in adsorbate-adsorbent interactions of various species and obstruction by the pore walls to some of the species in the mixture.

The existing adsorption theories such as Henry's law, Langmuir adsorption model and BET isotherm are incapable of predicting the adsorption isotherms of n-alkanes in zeolite pores. The reason is that in microporous adsorbents, the sorbate molecular mechanisms are influenced by geometrical constraints also. This limitation in the use of theory can be overcome by developing a molecular model and using computers to mimic the real system. This nature of simulation is called molecular simulations. With the development of advanced algorithms, improved force-field parameters and very high computational power of present day computers, molecular simulations have become an important tool in studying adsorption on micro-porous materials.

Adsorption experiments of mixtures of long chain alkanes into silicalite under liquid phase conditions show selectivity inversion and azeotrope formation.

These effects are due to the subtle interplay between the size of the adsorbed molecules and pore topology of the adsorbent. The underlying molecular mechanisms responsible for selective uptake of one of the components cannot be obtained from experiments but can be realized through simulations. Therefore, in this study, the selective uptake of lighter component during liquid phase adsorption of C_{14}/C_{15} and C_{15}/C_{16} n-alkane binary mixtures in the zeolite silicalite is understood through configurational bias grand canonical Monte Carlo (CB-GCMC) molecular simulation technique and a course-grained siting analysis. The simulations are conducted under conditions of low and high loading. The siting pattern of the adsorbates inside the zeolite pores is used to explain the selectivity as seen in experiments.